

SHOCK METAMORPHISM OF PETRURGICAL MATERIALS: SYNTHETIC MINERAL ALLOYS

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The shock-induced structural and morphological transformations in petrurgical materials are studied. Synthetic minerals serve as an example of petrurgical materials. An analogy is drawn between shock metamorphism in nature and shock action on synthetic material. The data obtained make it possible to study shock action as a new kind of synthesis.

Key words: shock metamorphism, shock minerals, dissipation, synthetic mineral alloys, mechanosynthesis.

It is known that the structure of many rocks was formed as a result of shock action (collision with a meteorite and so forth). Rare minerals, for example, unique polymorphic modifications of some minerals, which can arise only as a result of shock action, are found in direct-impact zones. Among such minerals are some modifications of quartz, such as stishovite and coesite.

It has been determined by the methods of experimental petrology that some impactites (shock modifications of minerals) can be obtained artificially by the action of an impact on a small volume of a material, where the force of the impact relative to the volume is comparable to the loads on geological formations at the moment of a collision with a meteorite.

Shock loads can change the structure not only of natural but also synthetic materials. Therefore, a shock can be regarded not only as a destructive action but also as a method of synthesis. This is already partially realized in the technology of mechanoactivation [3, 4].

This technology makes it possible to obtain powdered material with practically any composition and with an extremely finely disperse structure. However, the structural changes accompanying mechanoactivation differ from those due to a shock load on rock, since the target for the shock is a solid monolithic formation and not a powder. For this reason it is crucial to study the structural transformations induced by shock action on material in solid and monolithic states.

It is known that the phenomenon of dissipation of mechanical energy arises under a shock acting on a material, i.e., the energy of an impact starts to transform, as a rule, in

several stages and as a result of the transformation the energy of the impact transforms into heating [5].

Depending on the character of the structure different materials dissipate energy differently. A graphic example is the behavior of materials hit by a bullet from a firearm. If a material completely fractures when struck by a bullet and the bullet stops, then the kinetic energy of the bullet is practically completely expended on the fracture process and on structural transformations in the material; if the bullet does not stop, the material is not prone to dissipation. The more a material is prone to energy dissipation, the more its structure changes in the dissipation process.

Rocks are materials with a high dissipation capability. This is confirmed by the phenomenon of shock metamorphism described above. Since the dissipation capability depends on the character of the structure, it is obvious that materials whose structure resembles that of natural mineral formations will also possess a similar capability for dissipation.

Among the varieties of nonmetallic materials close to rocks are glass and ceramics, which are used for protective armor and not only against bullets but also other projectiles, for example, they protect turbomotors from detached blades and so forth [6].

However, materials showing even greater similarity to natural mineral formations do exist. These are petrurgical materials: synthetic mineral alloys (syminals). The term “syminals” came into use not too long ago. Previously, such materials were united by the term “stone casting,” i.e., they were named according to the production method.

Syminals comprise materials that are obtained by remelting and modifying a combined batch consisting of one or several rock varieties or technogenic mineral formations. In terms of their structure and composition syminals are

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close to basic and ultrabasic igneous rocks. All of them contain an amorphous phase from 2 to 30%, and the crystalline part of the structure ordinarily includes two or more mineral phases. The overwhelming majority of syminals contains approximately 50% SiO_2 . According to the laws of physics the structure of syminals can be regarded as a condensed medium.

The aim of the present research is to study the shock-induced structural transformations in syminals.

Syminals synthesized on the basis of hornblende raw material were studied. The chemical composition of the samples was established by means of x-ray spectral fluorescence using SRM-18 and EDX 900HS fluorescence spectrometers. The mass content of the components is as follows (wt.%): 9.91 MgO; 10.82 Al_2O_3 ; 49.6 SiO_2 ; 0.22 K_2O ; 10.33 CaO; 1.38 TiO_2 ; 0.54 Cr_2O_3 ; 0.16 MnO; 14.02 $\text{Fe}_2\text{O}_{3\text{tot}}$.

RESEARCH METHODS AND RESULTS

The material was subjected to shock in a high-velocity penetration setup [7]. The principle of operation consists of the following. The target (sample) is placed into the setup. The dissipative properties of the target material are to be determined. A penetrating projectile is shot at the sample. The projectile can have different shapes; its velocity can reach 850 m/sec. The magnitude and distribution of the temperature on the back surface of target is measured with a IR camera at the moment of impact. The impacts on the samples were made with a cylindrical impactor traveling with velocity 125, 600 and 800 m/sec.

After the collision the impactor stopped moving, and the sample completely fractured. This situation was observed in each test, but the size of the fragments depended on the velocity of the impactor.

The structural changes were evaluated by means of x-ray structural analysis and scanning electron spectroscopy with the associated spectral microprobe analysis.

An ESR70-30 DX/2 spectrometer was used for the x-ray structural analysis. A JSM-6390LV scanning electron microscope was used for scanning electron microscopy and microprobe analyses.

The impact-induced structural changes before and after the tests were determined using a spectrogram of the initial composition.

In the x-ray diffraction pattern of the sample which underwent a collision with velocity 125 m/sec the main phase is, just as before fracture, clinopyroxene with diopside-augite composition, a significant amount of olivine is present and quartz impurity remains and chromite traces are present. Of greatest interest from the standpoint of structural changes is a peak corresponding to a shock modification of quartz — *stishovite* (2.96 nm).

X-ray structural analysis of the syminal sample fractured at impactor velocity 650 m/sec showed an intensification of the stishovite peak. This is an indirect confirmation of the

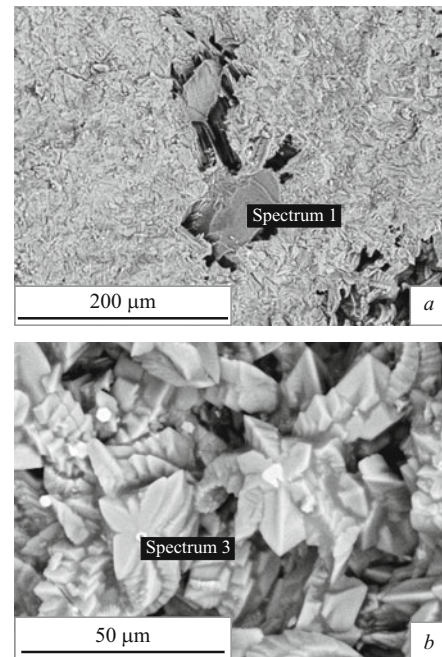


Fig. 1. The surface of a fragment of a sample fractured by an impactor with velocity 125 m/sec (a) and an enlarged section of the surface of a fragment of this sample (b).

impact origin of this component. In addition, broadening of all other peaks was observed; this corresponds to the appearance of shock-induced changes of pyroxenes.

Target fragments were taken for analysis by scanning electron microscopy.

An image of the surface of a sample fragment, fractured by an impactor at 125 m/sec, is presented in Fig. 1a.

Two characteristic zones stand out clearly. One zone has a distinct relief surface and the other has the form of a pitting fracture, more characteristic for materials with amorphous or close to amorphous structure. The fact that sections with different surface morphology are separated from one another by some distance is interesting. Probably, cracks formed between different phases in the course of the fracture process. It was determined that SiO_2 is the base (MgO, FeO all else) in the pitting fracture section. SiO_2 is also present on the crystalline fracture section, but in a much smaller amount. Albite, magnesite, alumina, wollastonite, feldspar and traces of iron and titanium oxides were also found.

The crystalline zone is nonuniform. For this reason it was studied more conveniently at high magnification (Fig. 1b). This revealed the following morphological features of the surface. The profile of the surface asperities is identical to the character of the crystal growth. This confirms that initially a crack formed directly on the interface of two disordered phases.

The asperities forming the relief have the same form and height; particles with different composition are found at the tips of the highest asperities. Spectral analysis was performed at a tip and on “notches” of crystalline asperities

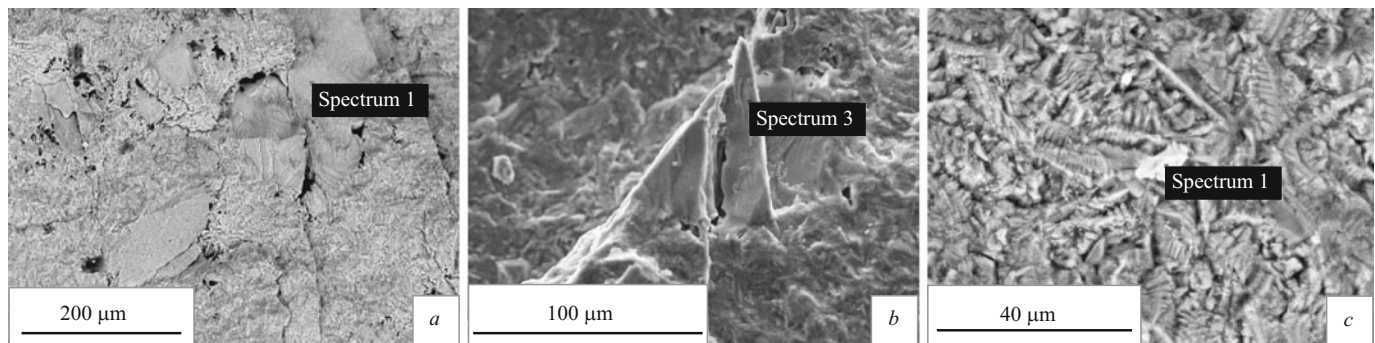


Fig. 2. Sections of the surface of a fragment of a sample fracture by an impactor at velocity 650 m/sec: *a*) overall view; *b*) zone with slip bands; *c*) zone of crystalline fracture.

(Fig. 2). It was determined that the base at the tips of the crystalline asperities is comprised of FeO , MgO and Al_2O_3 . The content consists of 6–7 wt.% Cr_2O_3 and small quantities of wollastonite, titanium oxide and silica. A different composition was found on the “notches” of the crystalline asperities; SiO_2 predominates, high content of MgO and CaO is noted in tandem with them, all other asperities are present in the same proportions, while chromium is completely absent.

Let us examine the difference of the fracture morphology and the composition of individual regions of the surface on samples fractured at high impactor velocities.

In a survey of the samples subjected to impact at 650 m/sec two characteristic zones were found on the fracture surface: one, just as in the past, is distinctly characteristic, and the exterior form of the other is outwardly reminiscent of a so-called typical “rupture zone” often encountered in fatigue tests of materials. Slip bands are observed on its surface (Fig. 2*a*). The cracks are more highly branched, but they show the same outline as crystalline aggregates and a clear displacement of some sections relative to others is observed. Nonuniformity is clearly seen on sections with slip bands while the relief in the crystalline zone shows a smaller difference of asperity heights, but asperities of a characteristic form, on whose tips an accumulation of a separate phase is seen, are present on it.

Spectral analysis showed that in sections with slip bands the base consists of SiO_2 and MgO with wollastonite and precipitates of the oxides MnO and FeO are present. A characteristic feature is the presence of manganese oxide, which is not seen in samples obtained under impact at lower velocity. An examination of the surface morphology of this zone at high magnifications (Fig. 2*b*) showed that it also exhibits clear differences from the fracture planes formed with lower fracture speeds. It is not planar but stepped, its composition is close to that on the surface of the pitting fracture in the first case, but wollastonite precipitate is observed at high fracture speeds.

The surface zone with crystalline relief (Fig. 2*c*) also differs in composition first and foremost by precipitation of a small amount of chlorine compounds. A more detailed study

of the relief in the crystalline zone reveals that the difference of the heights of the asperities is several-fold smaller. The surface is not so sharp-angled, and overall the crystallites are smaller than in the first case. The composition essentially did not change.

The most global changes in structure, surface morphology and composition of individual surface zones are found in a sample obtained with penetration at maximum velocity 800 m/sec. First, there is no pronounced cracking: instead of cracks of the fold it is likely that at this stage of the tests all cracks developed finally and the material fractured along all of them. Three zones stand out clearly: dark sections with flat morphology (Fig. 3), a crystalline section, whose relief is appreciably lower and consists of sections with lower dispersity, and crystallites present earlier on the tips, many of which increased appreciably in size.

A study of the composition of individual sections of the surface showed that the dark sections contain carbon, which was not the case before, and in addition carbon comprises their base while everything else consists of small amounts of all oxides encountered in the material as well as small sulfur inclusions.

Studies at high magnifications also showed that the crystallites containing chromium have an individual morphology (Fig. 4). First, it decomposed into components comprising

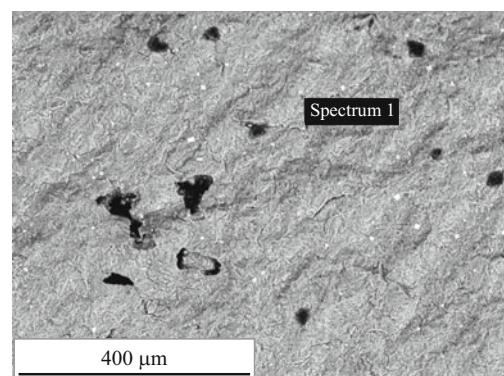


Fig. 3. Surface of a fragment of a sample fractured at velocity 800 m/sec, graphite precipitates on the fracture surface.

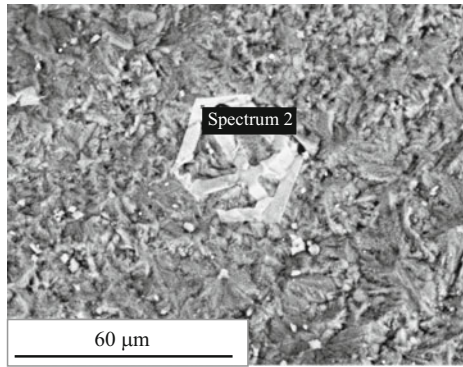


Fig. 4. Fracture and deformation of the structural components of syminal with penetration at velocity 850 m/sec.

the framework of the crystal skeleton, after which it deformed, its composition changed and a small amount of vanadium is found, which was not found previously. The size of the crystalline component decreased appreciably and evened out in height. The fold boundaries are clearly delineated at crack sites, crystallites are also clearly deformed and fragmented, their composition also changed, even though the composition once again contains silicon dioxide, the sodium oxide content increased considerably and chromium oxide appeared and clearly arrived from another phase as a result of fragmentation.

X-ray phase analysis and electron microscopy combined with microprobe analysis show unequivocally that shock metamorphism is present in syminals. However, since their base is a synthetic analog of pyroxene, which is quite resistant to impact effects, the changes consist of, first and foremost, not polymorphic transformations but rather removal and re-distribution of the elements between components.

Sodium and calcium are removed first. The silicon-dioxide concentration changes next. This is explained from the standpoint of the transition of a part of this component into stishovite, which expanded as a result of transformations, crumbled and was partially removed in this manner from the fragment.

The appearance of new elements in the analysis of samples attracts the greatest attention. Of greatest interest is the precipitation of carbon. To understand its origin it is necessary to turn to the process leading to the formation of syminals.

A carbon arc is used to put the initial material for the production of syminals into a melt state. Since the graphite electrode interacts with the melt, a significant fraction of its melted particles passes into melt. Since the syminal melt is similar to magma melt, it can be stated with confidence that the carbon dissolves well in it, forming a saturated solid solution of carbon in clinopyroxene. Under a shock load the removal of different elements, especially sodium, potassium and calcium and also carbon, as experience with syminal shows, is characteristic. This also explains the precipitation of vanadium in some phases. Carbon is not always present in

natural mineral formations, and hence it does not always precipitate in astroblemes in the process of shock metamorphism.

DISCUSSION

The data obtained make it possible to link all structural changes occurring in syminals during the dissipation of mechanical energy in the following sequence:

impact → polymorphic transformation of quartz into stishovite (swelling of quartz) → local heating and pressure on an aggregation of clinopyroxene by expanding stishovite → partial disordering of clinopyroxene → precipitation of sodium and calcium → precipitation of carbon, vanadium, sulfur and other elements from a solid solution and diffusion of chromium → disintegration into fine dust and fused particles.

Since in a collision elastic waves capable of displacing and consolidating structural defects, such as dislocations, arise initially in the body and heat release increases atomic vibrations, it is logical to suppose that the first phase to suffer is the one where long-range order is maintained least, i.e., in the amorphous phase. Initially, the low-temperature form of quartz (α -quartz), forming crystals of trigonal-trapezoidal form, is present in syminals. The characteristic units of quartz are tetrahedra, joined to one another along the edges. In all cases each silicon atom is surrounded by a tetrahedron formed by oxygen atoms. In accordance with the chemical composition of quartz the oxygen atoms along the edges of the tetrahedra belong to two tetrahedra simultaneously. The tetrahedra form nonplanar six-member rings in a crystal lattice. However, the basic structural element in amorphous silicon dioxide is likewise a SiO_2 tetrahedron, but eight-member planes of rings alternating at different angles are present together with the six-member rings [8].

Only Si–O bonds are present in quartz. They are equally homopolar and heteropolar. Thus, the representation of the components of the quartz crystal lattice in terms of Si and O atoms or Si^{4+} and O^{2-} ions reflects only the limiting cases of real chemical bonds. It leads to the possibility of homo- or heterolytic rupture of Si–O bonds under impact. Quartz in any of its states is a brittle material, and for this reason, as a rule, it disintegrates under impact. The experience with mechanosynthesis shows that shock-induced disintegration of quartz is similar to dissolution or melting. According to the phase diagram of quartz under a sharp impact conditions are created for a transformation of quartz into stishovite with the degree of crystallinity decreasing. The density of stishovite is lower density than that of the low-temperature modifications of quartz. At the moment of impact the oscillations of elastic waves resonate with oscillations of the quartz lattice, quartz swells as a result of the instantaneous pressure, stresses arise and relax because of cracks, but heating also occurs since not all energy goes into crack formation.

In a polymorphic transition in silicon oxide the pressure and temperature act on clinopyroxene even in microvolumes. The pressure force acting on the clinopyroxene crystallites can be quite large, so that according to high-pressure physics intensive amorphization starts in this phase. Na^+ and Ca^{2+} ions will be intensively removed from the amorphized phase, and the action of temperature will cause microparticles to fuse, as a result of which decomposition of aluminum-silicate tetrahedra will start in them.

This will unavoidably affect the phase containing chromite, which is distributed in clinopyroxene. Under the action of the changes in clinopyroxene this phase deforms and partially decomposes. As the intensity increases the changes bring about transformations in the clinopyroxene, which is a solid solution with carbon, and as a result pure carbon precipitates at the periphery of the crystallites.

CONCLUSIONS

The results of this research show that shock action on syminals has definite prospects.

1. The shock action promotes removal of alkali impurities, and the subsequent remelting of the powder after impact makes it possible to obtain higher-quality and pure syminals.

2. As a result of an impact solid particles of chromite can be detached for further use as a material with high hardness.

3. The precipitation of carbon in the form of a separate phase shows that with high velocities and changes in pressure it different polymorphic modifications of carbon can be prepared by shock metamorphism of syminals.

In summary, the shock-induced structural changes in syminals were studied and systematically described. It was proved theoretically that there are prospects for using shock action as a method of processing syminals in order to obtain unique products.

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